

PATENT SPECIFICATION

(11) 1 488 061

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- (21) Application No. 39422/75 (22) Filed 25 Sept. 1975
 (31) Convention Application No. 71012
 (32) Filed 26 Sept. 1974 in
 (33) Luxembourg (LU)
 (44) Complete Specification published 5 Oct. 1977
 (51) INT CL² A61K 7/42
 (52) Index at acceptance
 A5B771



C2C 1473 1673 213 220 226 22Y 246 253 25Y 290 29Y 305
 30Y 351 355 35Y 360 362 364 365 36Y 388 407 409
 40Y 500 509 50Y 623 624 625 634 652 662 672 675
 777 790 79Y UK WD WE

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(54) COSMETIC COMPOSITIONS CONTAINING DERIVATIVES OF 2-PHENYL-BENZOFURANE

(71) We, L'OREAL, a French Body Corporate, of 14 Rue Royale, Paris 8e, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to anti-sunburn compositions containing certain derivatives of 2-phenyl-benzofurane.

The use, as ultra-violet filters in cosmetic compositions, of 2-phenyl-benzofurane and of certain of its methyl derivatives, particularly with methyl groups in the 5, 6, 7, 2' and 4' position, is already known (see British Patent Specification No. 1,114,030); these compounds are effective in the absorption range of erythematous radiation.

The cosmetic compositions of the invention are capable of retarding the development of erythema caused by sunlight, without however inhibiting the pigmentation of the skin which, in addition to its aesthetic appeal, is the natural way of protection against harmful solar radiation.

It is, in fact, well-known that solar radiation which reaches the earth's surface can be broken down into 3 types of radiation:

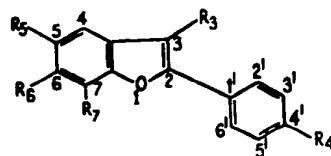
ultra-violet radiations,
 visual radiations, and
 infra-red radiations.

It is certain ultra-violet radiations (those of the highest energy) that are the cause of erythema caused by sunlight and which, if exposure is prolonged, can bring about severe burns and even cutaneous cancers.

In effect, the ultra-violet flux can itself be broken down into an erythematous flux (wavelengths of between 290 and 320 nm) which causes the appearance of the erythema which after a certain time (in general 2 to 5 days) will give rise to a natural pigmentation due to a photo-induced melanogenesis, and a non-erythematous bronzing flux (wavelength between 320 and 370 nm) which brings about an immediate pigmentation (appearance between 2 and 5 hours after the start of the exposure) due to a photo-oxidation of certain precursors of melanine present in the skin.

It is thus of interest to be able to retard the appearance of the erythema caused by sunlight and its development into burns, thus allowing a longer or more intense exposure (as is generally the case in the mountains) without counteracting the beneficial effect of natural bronzing.

The subject of the present invention is an anti-sunburn composition which conforms to the abovementioned advantages and contains, as the protective agent against actinic rays, in a cosmetic vehicle capable of forming a continuous film which can easily be spread over the epidermis, at least one compound having the general formula:



(I)

in which R_3 represents H , $-CO-R_1$ or $-CHOHR_1$, each of R_4 , R_5 , R_6 and R_7 independently represents H or $-O-R_2$, with the proviso that at least one of R_5 , R_6 , R_7 is other than H ,

R_1 represents CH_3 and

R_2 represents C_1-C_4 alkyl,

preferably in an amount of 0.05 to 10%, particularly 0.5 to 6%, by weight.

The compounds of the formula (I) exhibit an excellent absorption of ultra-violet radiation in the range of wavelengths of 290 to 320 nm (nanometres) as shown by the rapid decrease in the ratio (transmitted erythematous flux)/(incident erythematous flux) or

$$\frac{T}{\% \phi - E}$$

as a function of the concentration of the said compounds and of the choice of the solvent and of the ingredients contained in the composition which ensure the protection of the skin by forming a film, of thickness generally from 3 to 20 microns. The choice of the compounds of the formula (I), of the concentration used and of the cosmetic vehicle furthermore makes it possible to obtain a composition of the invention suitable for the protection of the various types of epidermis.

The abovementioned ratio has the advantage of directly showing the degree of protection against erythematous radiation for a given concentration and a given solvent or cosmetic vehicle, as shown by B. M. CUMPERLIK in J. Soc. Cosmet. Chem. 23, pages 333, (1972)).

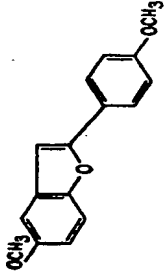
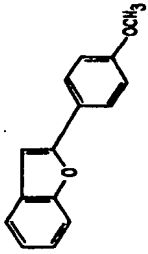
The Table which follows shows, in %, for a certain number of compounds of the formula (I) and for various concentrations C expressed in milligrams per 100 ml of methanol, firstly the value of the ratio

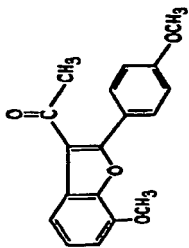
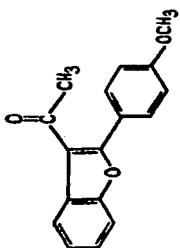
$$\frac{T}{\phi - E}$$

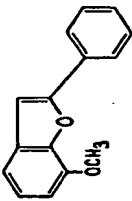
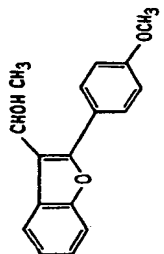
and secondly the value of the ratio (transmitted bronzing non-erythematous flux)/(incident bronzing non-erythematous flux) or

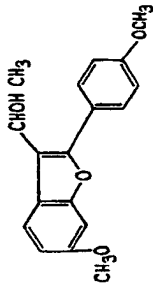
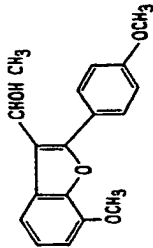
$$\frac{T'}{\phi - BNE}$$

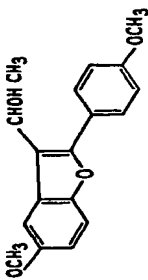
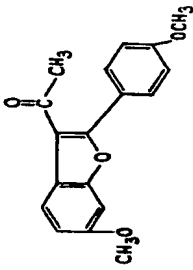
The measurements are in each case carried out in analysis cells across a thickness of 10 mm of solution of the product.

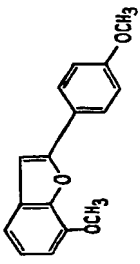
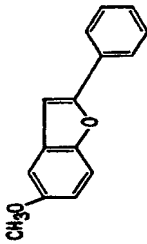
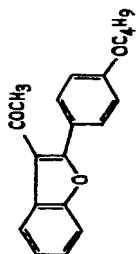
	Compounds	% ϕ T (Concentration C in mg/100 ml of methanol)				% ϕ T' BNE (Concentration C in mg/100 ml of methanol)			
		1	2	3	4	1	2	3	4
No.	Formula								
1		10.18	1.09	0.14	0.03	55.27	47.26	44.12	42.11
2		4.83	0.85	0.49	0.38	72.21	64.92	61.57	53.30

	Compounds	% ϕ T (Concentration C in mg/100 ml of methanol)				% ϕ T' BNE (Concentration C in mg/100 ml of methanol)			
		1	2	3	4	1	2	3	4
No.	Formula								
3		32.13	10.37	3.36	1.10	55.11	36.11	22.68	15.29
4		30.47	9.33	2.87	0.89	52.05	30.73	20.29	14.59

	Compounds	T % ϕ E (Concentration in mg./100 ml of methanol)				T, % ϕ BNE (Concentration in mg./100 ml of methanol)			
		1	2	3	4	1	2	3	4
5	Formula 	16.76	5.36	3.28	2.65	94.84	90.70	87.36	84.61
6		16.24	4.69	2.56	1.96	93.70	88.75	84.79	81.57

	Compounds	% ϕ T (Concentration in mg/100 ml of methanol)				% ϕ T' BNE (Concentration in mg/100 ml of methanol)			
		1	2	3	4	1	2	3	4
No.	Formula								
7		18.16	3.64	0.88	0.30	74.71	63.73	58.06	54.65
8		23.19	7.35	3.52	2.31	92.68	86.88	82.21	78.40

	Compounds	% ϕ T (Concentration in mg/100 ml of methanol)				% ϕ T' BNE (Concentration in mg/100 ml of methanol)			
		1	2	3	4	1	2	3	4
No.	Formula								
9		18.93	3.84	1.08	0.47	59.00	38.78	28.09	21.95
10		46.6	21.87	10.33	4.91	60.89	83.53	33.82	27.50

	Compounds	% ϕ E (Concentration in mg/100 ml of methanol)				% ϕ T' BNE (Concentration in mg/100 ml of methanol)			
		1	2	3	4	1	2	3	4
No.	Formula								
11		28.33	8.92	3.46	1.81	79.56	69.98	64.27	60.27
12		10.81	1.39	0.31	0.14	69.02	59.35	55.02	52.44
13		33.6	11.4	3.88	1.33	51.5	30.8	20.4	14.7

By a method analogous to that used for the determination of the transmitted percentages of the erythematous flux,

$$\frac{T}{\phi - E},$$

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using the filters in the wavelength range from 290 to 340 nm, it is also possible to determine the percentages of immediately bronzing or non-erythematous flux transmitted by these same filters in the range of wavelengths of 320 to 375 nm, and represented by

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$$\frac{T'}{\phi - \frac{T}{BNE}}.$$

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It is well-known that several types of anti-sunburn formulations exist which are suited firstly to the sensitivity of the epidermes to be protected and secondly to the intensity of the exposure. Hence it is necessary to choose, in accordance with the type of formulation desired, filters having appropriate values of the percentage

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$$\frac{T}{\phi - E}$$

and of the percentage

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$$\frac{T'}{\phi - \frac{T}{BNE}}.$$

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For example, to protect ultra-sensitive skins such as those which show allergies when exposed to the sun, compositions having very low values of the percentage

$$\frac{T}{\phi - E}$$

and of the percentage

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$$\frac{T'}{\phi - \frac{T}{BNE}}.$$

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will be used. In contrast, bronzing compositions intended for sensitive skins have a percentage

$$\frac{T}{\phi - E}$$

which is as low as possible and a percentage

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$$\frac{T'}{\phi - \frac{T}{BNE}}.$$

which is as high as possible.

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The compounds of the formula (I) of which the dermic toxicity is very low have satisfactory to good solubility in solvents or fatty products. As vehicles there may in particular be mentioned lanoline, petrolatum (Vaseline. [Registered Trade Mark]), glycerol, triglycerides of fatty acids, polyethylene glycols, oxyethyleneated fatty alcohols, fatty esters such as isopropyl palmitate, myristate or stearate, oleyl oleate and butyl stearate, animal, vegetable or mineral oils, fatty alcohols, glycerol mono-stearate and organic and inorganic waxes, being used in an amount of 1 to 97.5%, preferably 1 to 40%, by weight, of the composition. Isopropyl palmitate or isopropyl myristate are particularly suitable for the preparation of compositions which can be applied to the epidermis in the form of a continuous film of the desired thickness.

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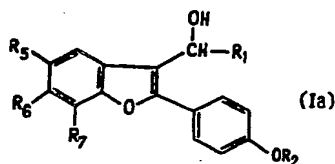
However, it is also possible to use as vehicle for the compounds of the formula (I)

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a C₁ to C₄ alcohol or an aqueous-alcoholic or oily-alcoholic vehicle or a propellant when the composition is to be aerosol-producing.

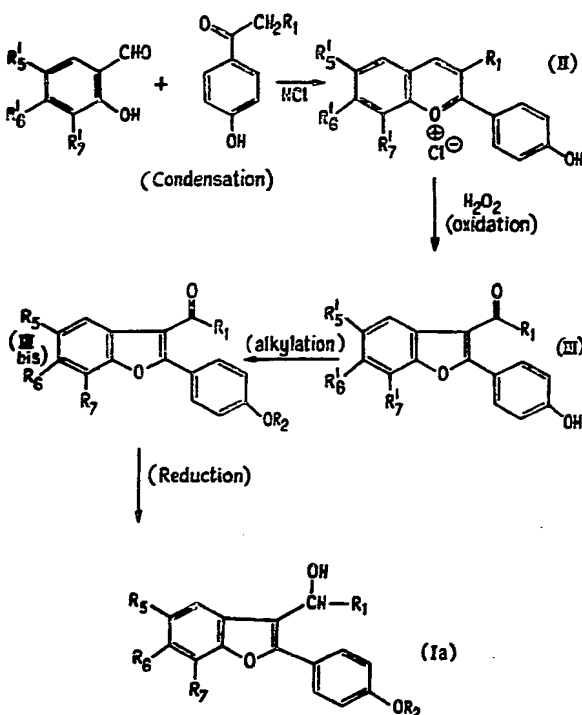
The compounds of the formula (I) are suitably used in the anti-sunburn cosmetic compositions of the invention at a concentration of 0.5 to 6%, preferably 1 to 5%, by weight relative to the weight of the composition, the compositions being in the form of, for example, lotions, sunoils or emulsions, aerosol-producing propellant-containing compositions in containers, gels, dispersions or suspensions.

In one embodiment of this invention, the composition contains a compound having the formula



in which R₄, R₅, R₆, R₇ and R₁ have the abovementioned values.

These compounds are believed to be novel and are the subject of our application No. 25440/76 (Serial No. 1,488,062). These compounds wherein R₄ represents OR₂ can be prepared by a four-stage process in accordance with the following scheme:

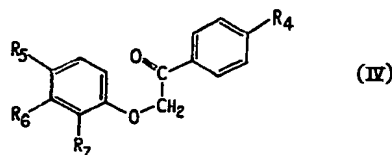


In this scheme, R₂, R₅, R₆, R₇ and R₁ have the abovementioned values. If R'₅, R'₆ and R'₇ represent H, R₅, R₆ and R₇ represent H and if R'₅, R'₆ and R'₇ represent —OR₂ or —OH, R₅, R₆ and R₇ represent —OR₂. Of course, if it is desired to prepare these novel compounds wherein R₄ represents H, it is clear that the alkyl phenone used in the condensation step of the above scheme must be unsubstituted and further that the alkylation step will only be necessary if any of R'₅, R'₆ and R'₇ represents —OH in order to convert such —OH group to —OR₂.

This above scheme comprises a condensation stage (1) which gives flavylum salts (II), an oxidation stage (2) which gives the compounds of the formula (III), an alkylation stage (3) which gives the compounds of the formula (III bis) and the reduction stage (4) which gives the compounds of the formula (Ia). The reduction

is suitably carried out with sodium borohydride in the presence of an alcohol containing 1 to 4 carbon atoms or with lithium aluminium hydride in suspension in an inert solvent such as diethyl ether, isopropyl ether or tetrahydrofuran.

The compounds of the formula (I) in which R₃ is hydrogen can be prepared by a known process of cyclisation and dehydration, in the presence of polyphosphoric acid, of the aryloxyacetophenones of the formula:



in which R₄, R₅, R₆ and R₇ have the abovementioned values, at least one of them not representing hydrogen.

This well-known process consists of heating, for a period of time and at temperatures which vary according to the compounds, a mixture of aryloxyacetophenone and polyphosphoric acid in a respective weight ratio of about 1:10, this reaction being accompanied by a rearrangement which gives a 2-aryl-benzofurane as the cyclisation product.

In a further embodiment of this invention, the composition contains a compound of the Formula (I), in which R₃ is hydrogen, prepared by cyclisation and dehydration of the compounds of the formula (IV), according to which an aryloxyacetophenone of the formula (IV) is heated in an inert solvent such as xylene or toluene under reflux in the presence of polyphosphoric acid used in amounts varying from half to one-tenth of the amounts usually employed, the reaction mixture being stirred appropriately.

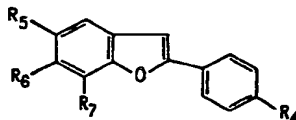
This process has numerous advantages compared to the usual process. On the one hand, it makes it possible to obtain a higher yield and on the other hand, because of the fact that it is carried out in a heterogeneous phase, it makes it possible easily to follow the progress of the reaction by a chromatographic or spectral analysis of a sample taken from the supernatant organic layer; also it makes it possible easily to isolate the product obtained at the end of the reaction.

In effect, it suffices to separate off the upper organic layer as soon as the analytical checks indicate the end of the reaction. Thereafter the lower phase is optionally taken up hot whilst stirring with an equal amount of the solvent used in the reaction. The supernatant layer is again separated off and combined with the upper layer previously separated off, and the whole of this organic phase is concentrated. The product can be isolated either by crystallisation or by vacuum distillation of the residue.

The Examples which follow, in which the percentages, unless stated otherwise, are to be read as being by weight, and the temperatures in degrees centigrade, further illustrate the present invention.

PREPARATIVE EXAMPLES.

A. Preparation of the 2-phenyl-benzofurane derivatives which are unsubstituted in position 3, and have the general formula:



in which R₄, R₅, R₆ and R₇ can have the values indicated for the formula (I) provided at least one of these does not represent hydrogen.

General method of working:

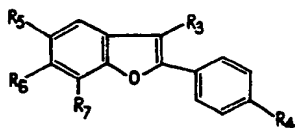
182 g of phosphorus pentoxide are added to 130 cm³ of phosphoric acid (d = 1.7), the addition being made in portions so as to avoid excessive exothermicity. After the last addition, the mixture is kept at 130° for 30 minutes whilst protecting it from moisture and ensuring good stirring. A solution which contains an aryloxy-acetophenone (from 80 to 400 g) in at least 1 litre of xylene, the solution having beforehand been heated under reflux and dehydrated, is then added. The whole is heated to the reflux

temperature for 5 hours whilst ensuring good stirring. After cooling, the xylene layer is separated off and the lower phase is taken up in about 500 ml of hot xylene whilst stirring efficiently for 15 minutes. The wash xylene is separated from the polyphosphoric acid and added to the xylene from the reaction. After concentrating the previously dried xylene solutions, the residue is crystallised from ethanol. This gives especially the compounds 1, 2, 5, 11 and 12 indicated in Table A below, the Table also showing the conditions of preparation, their melting point (M.p.) and the yield (Y) obtained.

TABLE A

No.	R ₄	R ₅	R ₆	R ₇	Heating time	$\frac{\text{Weight of polyphosphoric acid}}{\text{Weight of aryl-oxyacetophenone}}$	M.P. ϕ (°C)	Y (%)
5	H	H	H	OCH ₃	5 hrs	2	85°	65
12	H	OCH ₃	H	H	5 hrs	4	127°	60
2	OCH ₃	H	H	H	5 hrs	2	151°	58
1	OCH ₃	OCH ₃	H	H	5 hrs	2	163°	48
11	OCH ₃	H	H	OCH ₃	5 hrs	2	78°	15

B. Preparation of the 2-phenyl-benzofurane derivatives substituted in the 3-position by an acyl radical, and having the general formula:



in which R_4 , R_5 , R_6 and R_7 can have the values indicated for the formula (I) and R_3 is acyl.

(a) a solution containing 152 g (1 mol) of ortho-vanilline and 150 g (1 mol) of para-hydroxypropiophenone in 1 litre of ethyl acetate and 250 cm³ of absolute ethanol is saturated with hydrogen chloride gas whilst cooling the whole in an ice bath. The mixture is left to stand for 12 hours and the precipitate of a flavylum salt (II) obtained is filtered off, washed with ethyl acetate and dried in air.

(b) 300 g of the above flavylum salt (II) are dissolved in a mixture containing 3,000 cm³ of methanol and 3,000 cm³ of a buffer solution of pH 5.8. 600 cm³ of hydrogen peroxide of 30% strength by weight are added slowly to the mixture. The solution loses colour and a precipitate appears. The whole is left to stand for 1 hour and is diluted with 5 litres of water, whilst stirring. The precipitate formed is filtered off, washed with water and dried. Crystallisation from ethanol gives 185 g of 3-acetyl-2-(4'-hydroxyphenyl)-7-methoxy-benzofurane (III): Melting point = 222° C.

(c) a mixture containing 183 g of the above compound (III), 366 g of anhydrous potassium carbonate and 183 cm³ of methyl sulphate in 3,660 cm³ of anhydrous acetone is heated for 3 hours to the reflux temperature whilst maintaining good stirring. After cooling, the inorganic salts are filtered off and the filtrate is concentrated. The residue is treated with a dilute aqueous solution of potassium carbonate and the whole is stirred until a precipitate forms. The precipitate is filtered off, washed with water and dried. Crystallisation from methanol gives 136 g of 3-acetyl-7-methoxy-2-(4'-methoxyphenyl)-benzofurane (III bis). Melting point = 98° C. Yield = 70%.

Elementary analysis:

Compound No. 3: $C_{18}H_{16}O_4$ Theory % C 73.0 % H 5.44
Found 73.05 5.62

The compounds indicated in Table B below, which also shows their melting point M.p. and the yield obtained, are prepared by following an analogous procedure.

TABLE B

No.	R_3	R_4	R_5	R_6	R_7	M.P., (°C)	Yield (%)
(9)*	COCH ₃	OCH ₃	OCH ₃	H	H	115°	90
10	COCH ₃	OCH ₃	H	OCH ₃	H	77°	89
4	COCH ₃	OCH ₃	H	H	H	73°	85
13	COCH ₃	OC ₄ H ₉	H	H	H	70°	

(9)* = the intermediate in the synthesis of the compound No. 9.

The elementary analysis carried out on compounds No. 4, 10 and 13 give the following results:

5	<i>Compound No. 4:</i> $C_{17}H_{14}O_3$			
	Theory % C	76.7	% H	5.26
	Found	76.51		5.25
	<i>Compound No. 10:</i> $C_{18}H_{16}O_4$			
	Theory % C	73.0	% H	5.44
	Found	73.10		5.45
	<i>Compound No. 13:</i> $C_{20}H_{20}O_3$			
	Theory % C	77.9	% H	6.5
	Found	78.24		6.72

C. Preparation of the 3-(α -hydroxyalkyl)-2-aryl-benzofuranes having the formula:



in which R_4 , R_5 , R_6 and R_7 can have the values indicated for the formula (I) and R_3 is α -hydroxyalkyl.

Preparation of 3- α -hydroxyethyl-7-methoxy-2-(4'-methoxyphenyl)-benzofurane.

15 A solution containing 17.5 g of sodium borohydride in 200 cm³ of methanol is added slowly to a solution containing 75 g of 3-acetyl-7-methoxy-2-(4'-methoxyphenyl)-benzofurane (III bis) in 400 cm³ of methanol. The whole is heated to reflux temperature whilst stirring for 5 hours. Thereafter the solvent is driven off and the residue is taken up in 200 cm³ of water whilst stirring. The precipitate formed is filtered off and washed copiously with water. Crystallisation from alcohol gives 54 g of 3-(α -hydroxyethyl)-7-methoxy-2-(4'-methoxyphenyl)-benzofurane (Ia): Melting point = 100° C. Yield = 72%.

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Elementary analysis:

25	<i>Compound No. 8:</i> $C_{18}H_{18}O_4$			
	Theory % C	72.6	% H	6.05
	Found	72.75		6.29

The compounds indicated in Table C below, which also shows their melting point (M.p.) and the yield obtained, are prepared by an analogous procedure.

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TABLE C

No.	R_3	R_4	R_5	R_6	R_7	M.p., (°C)	Yield (%)
6	CHOHCH ₃	OCH ₃	H	H	H	78°	80
9	CHOHCH ₃	OCH ₃	OCH ₃	H	H	60°	75
7	CHOHCH ₃	OCH ₃	H	OCH ₃	H	98°	93

The elementary analysis carried out on the compounds 6, 7 and 9 gave the following results:

30	<i>Compound No. 6:</i> $C_{17}H_{16}O_3$			
	Theory % C	76.2	% H	5.98
	Found	76.13		5.86
	<i>Compound No. 7:</i> $C_{18}H_{18}O_4$			
	Theory % C	72.6	% H	6.05
	Found	72.62		6.24
35	<i>Compound No. 9:</i> $C_{18}H_{18}O_4$			
	Theory % C	72.6	% H	6.05
	Found	72.51		6.12

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The compounds 6, 7, 8 and 9 are new and are among those claimed in our application No. 25440/76 (Serial No. 1,488,062).

EXAMPLES OF SUNLIGHT FILTER COMPOSITIONS.

Example 1: Sun oil.

5	Compound No. 7	2 g	5
	Perfume	0.5 g	
	Tert.-butyl-para-cresol	0.0625 g	
	Colza oil q.s.p.	100 g	

10 In this Example, the compound No. 7 can be replaced by an equal weight of the compounds No. 4, No. 6 or No. 8. 10

Example No. 2: Sun lotion

	Propyl gallate	0.0625 g	
	Triglycerides of C ₈ —C ₁₂ fatty acids	40 g	
15	Compound No. 6	3 g	
	Benzyl salicylate	4 g	15
	Alcohol, 96° strength, q.s.p.	100 g	

In this Example, the compound No. 6 can be replaced by an equal weight of the compounds No. 4, No. 7 or No. 8.

Example No. 3: "Oil" aerosols.

20	Absolute alcohol	32 g	20
	Isopropyl myristate	23 g	
	Castor oil	2 g	
	Perfume	1 g	
25	Compound No. 4	2 g	
	Freon 12 ("Freon" is a Registered Trade Mark) (CCl ₂ F ₂)	40 g	25

The compound No. 4 can be replaced by an equal weight of compounds No. 6, No. 7 or No. 8.

Example No. 4: Aerosol foam.

30	The following active composition is prepared:		30
	Stearic acid	1 g	
	Triglycerides of C ₈ to C ₁₂ fatty acids	50 g	
	Oleyl alcohol	2 g	
35	Triethanolamine	1 g	
	Crosslinked polyacrylic acid	0.5 g	35
	Perfume	0.5 g	
	Propyl para-hydroxybenzoate	0.3 g	
	Compound No. 8	2 g	
	Water, q.s.p.	100 g	

40 In this composition, the compound No. 8 can be replaced by an equal weight of the compounds No. 4, No. 6 or No. 7. 40

For pressurisation, 90 g of the mixture described above are employed with 10 g of Freon 12.

Example No. 5: Softening and filtering "spray" (a sprayable product).

45	Cacao butter	10 g	45
	Compound No. 1	2 g	
	Isopropyl myristate	25 g	
	Nordihydroguaiaretic acid or "NDGA"		
50	prepared by ROCHE	0.005 g	50
	Perfume	0.8 g	
	Triglycerides of C ₈ —C ₁₂ fatty acids, q.s.p.	100 g	

For pressurisation, 50 g of this composition are taken and mixed with 30 g of Freon 12 and 20 g of Freon 114 (CClF₂—CClF₂).

55 The compound No. 1 can be replaced by an equal weight of the compounds No. 4, No. 6, No. 7, No. 8 or No. 12. 55

Example No. 6: Water-free sun oil.

	Vaseline, Codex	45 g	
	Vaseline oil, Codex	25 g	
	Polyvinyl stearate	5 g	
5	Micro-crystalline wax	10 g	5
	Lanoline	2 g	
	Propyl gallate	0.05 g	
	Ground nut oil	10 g	
	Perfume	0.8 g	
10	Compound No. 12	2 g	10

Compound No. 12 can be replaced by an equal weight of the compounds No. 1, 4, 6, 7 or 8, and a fat-soluble dyestuff can be introduced into the formula.

Example No. 7: Sun cream for dry skins.

	Triglycerides of C ₈ —C ₁₂ fatty acids	30 g	
15	Glycerol monostearate	6 g	15
	Stearic acid	2 g	
	Cetyl alcohol	1.2 g	
	Lanoline	4 g	
	Silicone oil	1 g	
20	Methyl para-hydroxybenzoate	0.3 g	20
	Propylene glycol	2 g	
	Triethanolamine	0.5 g	
	Compound No. 7	3 g	
	Perfume	0.5 g	
25	Water, q.s.p.	100 g	25

In this Example, the compound No. 7 can be replaced by an equal weight of the compounds No. 1, No. 4, No. 6, No. 8 or No. 12.

Example No. 8: Sun cream for normal skins.

	Cetyl stearyl alcohol oxyethylenated with 9 mols of ethylene oxide	2 g	
30	Glycerol monostearate	4 g	30
	Cetyl alcohol	4 g	
	Vaseline oil	10 g	
	Isopropyl myristate	5 g	
35	Propylene glycol	7 g	35
	Natural thickening polysaccharide	0.5 g	
	Butyl parahydroxybenzoate	0.3 g	
	Perfume	0.4 g	
	Compound No. 6	2.5 g	
40	Water, q.s.p.	100 g	40

The compound No. 6 can be replaced by an equal weight of the compounds No. 1, No. 4, No. 7, No. 8 or No. 12.

Example No. 9: Sun milk for normal skins.

	Oleyl cetyl alcohol oxyethylenated with 25 mols of ethylene oxide	5 g	
45	Vaseline oil	6 g	45
	Isopropyl myristate	3 g	
	Silicone oil	1 g	
	Cetyl alcohol	1 g	
50	Glycerol	20 g	50
	Methyl para-hydroxybenzoate	0.3 g	
	Perfume	0.3 g	
	Compound No. 7	1.5 g	
55	Water, q.s.p.	100 g	55

In this Example, the compound No. 7 can be replaced by an equal weight of compounds No. 1, No. 4, No. 6, No. 8 or No. 12.

Example No. 10: Lipstick.

	Cacao butter	10 g	
	Ozokerite	20 g	
	Compound No. 8	5 g	
5	Paraffin wax	4.9 g	5
	Oleyl alcohol	6 g	
	Castor oil	8 g	
	Propyl gallate	0.05 g	
	Lanoline	8 g	
10	Titanium oxide	2 g	10
	Perfume	0.5 g	
	Vaseline oil, Codex q.s.p.	100 g	

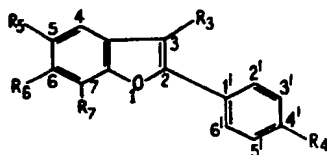
In this Example, the compound No. 8 can be replaced by an equal weight of the compounds No. 1, No. 4, No. 6, No. 7 or No. 12.

15 The perfumes used in Examples 1 to 10 above are chosen from amongst the perfumes usually employed in anti-sunburn compositions. 15

WHAT WE CLAIM IS:—

1. A composition suitable for application to the skin which comprises at least one compound of the general formula:

20



20

in which:

25 R_3 represents H , $—CO—R_1$ or $—CHOHR_1$, each of R_4 , R_5 , R_6 and R_7 , independently represents H or $—O—R_2$, with the proviso that at least one of R_3 , R_4 , R_5 , R_6 and R_7 is other than H , R_1 represents CH_3 and R_2 represents alkyl containing 1 to 4 carbon atoms, 25

and a vehicle which can form a continuous film and can easily be spread on the skin.

2. A composition according to Claim 1 which comprises 0.05 to 10% by weight of compound of formula (I).

30 3. A composition according to Claim 2 which comprises 0.5 to 6% by weight of compound of formula (I). 30

4. A composition according to Claim 3 which comprises 1% to 5% by weight of compound of formula (I).

5. A composition according to any one of Claims 1 to 4 which is in the form of a solution, a gel, an emulsion, a dispersion or a suspension, a lotion, an oil, a wax or an aerosol. 35

6. A composition according to any one of Claims 1 to 5 which contains at least one of lanoline, petrolatum, glycerol, a triglyceride of a fatty acid, a polyethylene glycol, an oxyethyleneated fatty alcohol, isopropyl palmitate, myristate or stearate, oleyl oleate or butyl stearate, an animal, vegetable or mineral oil, a fatty alcohol, glycerol monostearate, and an organic or inorganic wax, in an amount from 1 to 40% by weight. 40

7. A composition according to any one of Claims 1 to 6, in which the vehicle is water, a C_1 to C_4 alcohol, or an aqueous-alcoholic or oily-alcoholic mixture.

8. A composition according to Claim 7 in which the alcohol is ethanol. 45

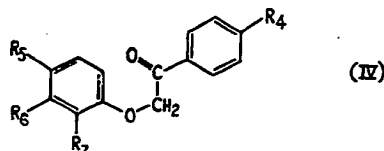
9. A composition according to any one of Claims 5 to 8 which is in the form of an emulsion and the oily phase contains one or more of a triglyceride of a fatty acid, oleyl alcohol, glycerol monostearate, cetyl alcohol, lanoline, silicone oil, petrolatum oil, isopropyl myristate or glycerol. 45

10. A composition according to any one of Claims 5 to 8 which comprises one or more of colza oil, cacao butter, a triglyceride of a fatty acid, isopropyl myristate, petrolatum oil, petrolatum polyvinyl stearate, micro-crystalline wax, lanoline, ozokerite, castor oil, paraffin or oleyl alcohol. 50

11. A composition according to any one of claims 5 to 10, which contains a propellant and is enclosed in aerosol-producing container.

12. A composition according to any one of the preceding claims in which R_3 represents a hydrogen atom or an acetyl or methyl hydroxy methyl radical.

13. A composition according to Claim 12, in which R_3 represents a hydrogen atom and the compound of formula I has been prepared by heating an aryloxyacetophenone of the formula:



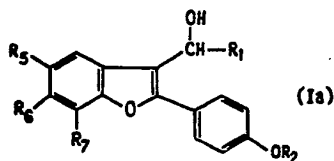
in which R_4 , R_5 , R_6 and R_7 are as defined in Claim 1, whilst stirring, in an inert solvent under reflux in the presence of polyphosphoric acid, and recovering the 2-phenyl-benzofurane derivative, after stopping the stirring, from the supernatant organic phase, and extracting the lower phase with said inert solvent.

14. A composition according to Claim 13, in which the solvent used in preparing the compound of formula (I) is xylene or toluene.

15. A composition according to Claim 13 or 14, in which the compound of formula (I) has been prepared by heating the aryloxyacetophenone and the polyphosphoric acid in a weight ratio from 1:1 to 1:5.

16. A composition according to any one of the preceding Claims in which at least one of R_4 , R_5 , R_6 and R_7 represents a hydrogen atom or a methoxy radical.

17. A composition according to any one of Claims 1 to 12 in which the compound (I) is of formula:



in which R_4 , R_5 , R_6 and R_7 are as defined in claim 1.

18. A composition according to Claim 17 in which at least one of R_4 , R_5 , R_6 and R_7 represents hydrogen or a methoxy radical.

19. A composition according to Claim 18 in which the compound (I) is 3-(α -hydroxyethyl)-7-methoxy-2-(4'-methoxyphenyl)-benzofurane.

20. A composition according to Claim 18 in which the compound (I) is 3-(α -hydroxyethyl)-2-(4'-methoxyphenyl)-benzofurane.

21. A composition according to Claim 18 in which the compound (I) is 3-(α -hydroxyethyl)-5-methoxy-2-(4'-methoxyphenyl)-benzofurane.

22. A composition according to Claim 18 in which the compound (I) is 3-(α -hydroxyethyl)-6-methoxy-2-(4'-methoxyphenyl)-benzofurane.

23. A composition according to Claim 1 substantially as hereinbefore described.

24. A composition according to Claim 1 substantially as described in any one of Examples 1 to 10.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1977.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.